

# Aperiodic optical coatings for neutral-color semi-transparent organic photovoltaics

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**Abstract:** Semi-transparent organic photovoltaics (ST-OPVs) have the potential for integration with windows for ubiquitous power generating applications. Typically, such applications require that ST-OPVs be neutrally transparent across the visible, and exhibit both a high average photopic transmittance (APT) and color rendering index, as well as iso-energetic chromaticity coordinates. In this work, we demonstrate the design and use of optical coatings to achieve ST-OPVs with neutral visible transmittance of APT = 50%, power conversion efficiency of 8.3%, and optical properties that are independent of a  $\pm 30^\circ$  variation in the solar angle of incidence. These simple optical coatings are rapidly designed using a genetic algorithm and transfer matrix formalism.

Due to the relatively high oscillator strengths of organic semiconductors,<sup>1</sup> the photoactive layers of organic photovoltaics (OPVs) can be thin, and yet absorb a significant fraction of the incident radiation within the relatively narrow absorption bands of the molecular excited states of the organic materials of which they are comprised. Hence, semitransparent OPVs (ST-OPVs) can utilize materials that are highly absorbing in the “invisible” infrared absorption bands, but only weakly absorbing in the visible.<sup>2–4</sup> These devices have several potential applications including integration with windows on buildings and automobiles.<sup>5–8</sup> In such applications, the human perception of light transmitted through the ST-OPV should be as close as possible to that of natural sunlight.<sup>7</sup> Ideally, this requires the device to exhibit a perceived neutral transmittance across the visible, a high color rendering index (CRI) at a correlated color temperature (CCT) of the solar disc of 5780 K, and close to isoenergetic Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of (0.33, 0.33). In practice, however, the ST-OPV transmittance spectrum is not neutral since the absorption spectrum of the organic active layer is not usually flat over the visible wavelengths. This results in ST-OPVs exhibiting colored transmitted light,<sup>5,9</sup> which is undesirable in most window applications.

In this work, we utilize a combination of genetic algorithm (GA) optimization<sup>10–12</sup> and transfer matrix calculations<sup>13–17</sup> to efficiently design multilayer thin film coatings to optimize ST-OPVs whose transmission spectra are close to that of natural sunlight. The optimization gives the ST-OPV a high and flat transmittance spectrum within the visible while increasing its power conversion efficiency (PCE) by reflecting near infrared (NIR) photons, allowing them a second pass through the active layer where they can be absorbed. In anticipation of window applications, the device must be resilient to relatively large changes in the solar angle of incidence (approximately  $\pm 30^\circ$ ) to maintain high efficiency during the diurnal and annual solar cycles.

Forward calculations are often employed to achieve optical outcoupling structures that improve the average photopic transmittance (APT).<sup>3</sup> One drawback to this method is that it is difficult to optimize the outcoupling structure for an arbitrary combination of film number, compositions, and thicknesses, since one has to calculate for all combinations and permutations of these three parameters and then select the optimum. As the number of layers increases, this becomes computationally arduous. Betancur, et al. previously reported optical coatings employing inverse solutions to calculate all possible outcomes of optical coatings for a given set of parameters.<sup>9</sup> This technique becomes increasingly inefficient as the number of thin film layers, and the optimization criteria expand. Here, we solve the inverse problem by stipulating the target transmittance of the ST-OPV, and then seeking the optimal optical thin film structure to achieve that result. Our method is both efficient and general. To test our assumptions, we fabricated an archetype OPV based on a non-fullerene acceptor and a polymer donor, and find that our target experimental optical outcoupling/reflection structure is achieved based on the computational algorithms and fitness criteria.

The transmittance spectrum of light propagating through a stack of thin films can be calculated using transfer matrix formalism and can be tailored by varying the thicknesses and numbers of the layers within the stack<sup>13</sup>. The thicknesses of the layers comprising the coating for ST-OPVs are targeted to achieve ~50 % neutral transmittance from 400 to 650 nm. This inverse calculation solves for the layer thicknesses once their number and refractive indexes are chosen. We define the target transmittance as the fitness function that is approached using a genetic algorithm that improves on successive populations (i.e. generations) of possible coatings until an optimum is achieved.

A more detailed discussion of our optimization routine is provided in the supplementary information. In essence, a population of possible coatings is established, each consisting of  $n$  thin film layers with thicknesses initially assigned by the GA. For each stack within this population, the transmittance of the full device is calculated, and is used as input for evaluation against a set of target parameters; *viz.*, transmittance, APT, and CIE. The algorithm then scores the optical performance of the device against these parameters and updates the thicknesses of the layers within stacks (forming a new population of stacks). The process is repeated until the optimal thicknesses of the layers is asymptotically approached, as determined by the value of the fitness parameter.

The ST-OPV active layer comprises a 2:3 (wt/wt) blend of the polymer donor, poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-)-2-carboxylate-2,6-diyl)] (PCE-10), and the non-fullerene acceptor (NFA), 4,4',10,10'-tetrakis(4-hexylphenyl)-5,11-bis(2-ethylhexyloxy)-4,10-dihydrodithienyl[1,2-*b*:4,5-*b'*]benzodithiophene-2,8-diyl)bis(2-(3-oxo-2,3-dihydroinden-5,6-dichloro-1-ylidene)malononitrile) (BT-CIC). Device A shown in Fig. 1(a) by the dotted rectangle, lacks outcoupling and reflecting layers. It was fabricated on a glass substrate with the following structure: indium tin oxide (ITO) (145 nm)/ ZnO (30 nm)/active layer (90 nm)/ MoO<sub>x</sub> (20 nm)/ITO (140 nm). The glass substrate with 2 mm wide patterned ITO cathode (sheet resistance of 15 Ω/sq) was commercially acquired from Luminescence Technology Corp. (Lumtec). The ZnO solgel precursor was spin-coated onto the ITO side of the substrate and annealed at 160 °C in air for 30 min. A solution of the active layer was spin-coated on the ZnO followed by deposition of MoO<sub>x</sub> by vacuum thermal evaporation (VTE) at a rate of 0.5 Å/s in a chamber with a base pressure of 1x10<sup>-7</sup> torr. Finally, the ITO anode of the device was deposited through metal shadow mask having the same pattern as the cathode but oriented orthogonally to the cathode resulting in a device area

of 4 mm<sup>2</sup>. The anode was deposited by magnetron sputtering at a rate of 1.7 Å/s in a chamber with a base pressure of 1x10<sup>-7</sup> torr.

The GA optimization routine was implemented to determine the thicknesses of the layers of the optical coating comprising aperiodic, alternating layers of MgF<sub>2</sub> and 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP) stacked above the anode. The optimal coating was determined to be MgF<sub>2</sub> (38 nm)/CBP (59 nm)/ MgF<sub>2</sub> (61 nm)/CBP (42 nm)/ MgF<sub>2</sub> (103 nm) and were deposited onto the anode of Device B, shown in Fig. 1(a). The refractive indices of the optical coating materials used as calculation inputs (MgF<sub>2</sub>, CBP, and ZnS) are shown in the inset, Fig. 2. The materials have almost constant refractive indexes from 400 – 1000 nm, negligible extinction coefficient, and significant index contrasts, making them suitable for broadband optical outcoupling coatings.

To ensure optimal outcoupling while also reflecting NIR photons back into the active layer, a third Device C, was fabricated. Its structure is shown in Fig. 1(b) consisting of a distributed Bragg reflecting (DBR) stack made of four pairs of alternating 90 nm ZnS and 161 nm of MgF<sub>2</sub> grown on top of the anode of the uncoated device followed by two pairs of aperiodic CBP-MgF<sub>2</sub> layers with thicknesses determined by GA. In all of the devices, the thickness of each layer was measured by ellipsometry.

The current density-voltage (*J-V*) characteristics of Devices A, B, and C were measured using a semiconductor parameter analyzer under 1 sun intensity (100 mW/cm<sup>2</sup>), simulated AM1.5G illumination. The external quantum efficiencies (EQE) of the devices were measured using a white light source and a monochromator at wavelength steps of 5 nm and a Si reference detector calibrated by Newport Corporation according to American Society for Testing and Materials (ASTM) standards E948-09 and E1021-06, for *J-V* and quantum efficiency

measurements, respectively. The transmittance spectra of all the devices were measured using a Perkin Elmer UV-VIS spectrophotometer.

The transmittances of Devices B and C are more neutrally transparent within the visible than Device A. This can be seen in Fig. 2, where the transmittances of Devices B and C show negligible wavelength dependence between 400 – 650 nm compared to Device A. Figure 3(a) shows the  $J$ - $V$  characteristics of the devices. The  $J$ - $V$  characteristics of Devices A and B coincide, indicating that the optical structure employed for B does not degrade performance. In contrast, the short circuit current density ( $J_{sc}$ ) of C is larger than either A or B due to recycling of NIR photons. The consequence of this reflection is evident in Fig. 3(b) where Device C exhibits a higher external quantum efficiency (EQE) in the NIR compared to the other two devices.

Figure 4 shows the variation in transmittance as a function of light incidence angle for Devices B and C. Both devices show little change for angles up to  $\pm 30^\circ$ . This is also apparent in Fig. 5 where the shift in CIE coordinates for both devices is negligible up to angles of  $30^\circ$ .

The PCE, APT and light utilization efficiencies, LUE, which is the product of PCE and APT, for each of the three devices are given in Table 1. The uncoated device has  $\text{PCE} = 5.9 \pm 0.2\%$  while Devices B and C have  $\text{PCE} = 6.1 \pm 0.1\%$  and  $8.3 \pm 0.1\%$  respectively. The APT of the uncoated device is improved by the optical coatings from 44% to 49% for B, and 46% for C. Thus, the LUE of the uncoated device increases from 2.6% to 3.0% for B, and 3.8% for C.

The variation of the optical properties of the devices with respect to angle of incidence is given in Tables 2 and 3 for Devices B and C, respectively. Within the 400 – 650 nm wavelength range, the transmittance spectrum of the uncoated device indicates a noticeable green tint with CCT = 5214 K and CRI = 88, and chromaticity coordinates of (0.34, 0.36). In contrast, transmittance of Device B is neutral between 400 – 650 nm. Figure 3 and Table 1 show that the

performance of the Device B is slightly improved from A as a result of the optical coating. At normal incidence, B has APT = 49%, CCT = 5599 K, CIE = (0.33, 0.36), and CRI = 89, values that are largely independent of the angle of incidence. Further, the chromaticity coordinates of B fall well within the zone where the color is perceived to be neutral and remain within an area of the size of a typical MacAdam ellipse for changes in incidence angle of  $\pm 30^\circ$ . Therefore, there is no noticeable change in the color of objects throughout the day. Similarly, at normal incidence, Device C has APT = 46% and CRI = 86, with the other values identical to Device B. For both B and C, these values remain unchanged for angles of incidence ranging from  $0^\circ$  to  $\pm 30^\circ$ .

The 400 – 650 nm transmittance spectral band of Device C, and its independence to changes in angle, are similar to those of B. The coating design employed for C (i.e., DBR + aperiodic layers) serves as a bandpass filter. This ensures that the interiors of buildings are shielded from thermal as well as harmful ultraviolet (UV) radiation. The short circuit current density of Device C is higher than both the uncoated device and Device B due to the recycling of NIR photons. The active layer employed for all the three devices primarily absorbs between 600 and 900 nm, as apparent from the EQE spectra in Fig. 3(b). The reflection of the NIR photons in Device C gives rise to the increased EQE and hence the improvement in  $J_{sc}$ . Therefore, Device C achieves PCE = 8.3%, or 41 % and 36 % improvement over A and B, respectively. Also, C has an LUE = 3.8 %, which is the highest among the three devices. Although the shifts in CIE coordinates with change in angle of incidence are small for both Devices B and C, the CIE coordinates of Device C shifts more than those of Device B due to the relatively narrow passband of the DBR.

In conclusion, have demonstrated the use of GA and transfer matrix formalism to design and implement aperiodic thin film coatings for ST-OPV to achieve high neutral transmittance and

increased PCE. The optimization scheme used to design the coatings is not only simple and computationally efficient, but robust since the genetic algorithm proceeds by improving upon the parameters of a given ‘possible’ solution so that a subsequent solution is better than the one that precedes it<sup>11</sup>. The process also employs a minimal computational time since there is no need to try out all of the possible combinations of the optical structures to achieve an optimum. The devices coated with the thin film show resilience to changes in their optical properties for up to  $\pm 30^\circ$  variation from the normal angle of incidence, which is important ST-OPVs for window applications.

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**Data Availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Supplementary Material**

A description of the genetic algorithm and transfer matrix methods is provided.

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TABLE 1. Operating characteristics of ST-OPV under simulated AM 1.5G, 100 mW/cm<sup>2</sup>, illumination.

	$J_{sc}$	$V_{oc}$	$FF$	$PCE$	$APT$	$LUE$
	[mA/cm <sup>2</sup> ]	[V]	[%]	[%]	[%]	[%]
Device A (uncoated)	14.4±0.3	0.68±0.01	60.0±1.0	5.9±0.2	44	2.6
Device B	14.2±0.1	0.68±0.01	62.7±0.1	6.1±0.1	49	3.0
Device C	18.6±0.1	0.67±0.01	66.0±0.3	8.3±0.1	46	3.8

TABLE 2. Optical characteristics of Device B.

	Uncoated device (normal incidence)	normal incidence	15 <sup>0</sup>	30 <sup>0</sup>	45 <sup>0</sup>	60 <sup>0</sup>
APT (%)	44	49	49	47	45	38
CCT (K)	5214	5599	5599	5599	6007	6073
CIE	(0.344, 0.363)	(0.330, 0.364)	(0.329, 0.363)	(0.328, 0.362)	(0.325, 0.355)	(0.319, 0.344)
CRI	88	89	89	90	91	91

TABLE 3. Optical characteristics of Device C.

	normal						
	incidence	10 <sup>0</sup>	20 <sup>0</sup>	30 <sup>0</sup>	40 <sup>0</sup>	50 <sup>0</sup>	60 <sup>0</sup>
APT (%)	46	46	45	43	40	35	28
CCT (K)	5599	6038	6038	6038	7649	6987	3623
CIE	(0.327, 0.359)	(0.323, 0.352)	(0.321, 0.351)	(0.317, 0.352)	(0.308, 0.353)	(0.300, 0.349)	(0.292, 0.341)
CRI	86	86	84	81	76	70	66

## Figure captions

FIG. 1: Structures of Devices (a) B and (b) C with the uncoated Device A indicated by with the dashed rectangle in (a).

FIG. 2: Transmittance spectra of Devices B and C are flatter in the wavelength range of 400 – 650 nm than that of Device A. *Inset*: Indexes of refraction of  $\text{MgF}_2$  (solid curve), CBP (dotted curve) and ZnS (dashed curve) used to calculate the layers thicknesses of the coatings.

FIG. 3: (a) Current density – voltage characteristics of Devices A, B, and C. (b) External quantum efficiencies (EQE) spectra of Devices A, B, and C.

FIG. 4: Angle dependent transmittance spectra of (a) Device B and (b) C showing insensitivity to  $\pm 30^\circ$  deviation in illumination from normal incidence.

FIG. 5: Shifts in the CIE coordinates of (a) Device B and (b) C with incidence angle. The coordinates stay within a small area of the CIE space for all incidence angles for both devices. For clarity, only a small portion of the CIE color space and color temperatures is shown.